High-rate reactive ion etching of barium hexaferrite films using optimal CHF\textsubscript{3}/SF\textsubscript{6} gas mixtures

Zhaohui Chen,\textsuperscript{1,*} Aria Yang,\textsuperscript{1} Changqing Xie,\textsuperscript{2} Qinghua Yang,\textsuperscript{2} C. Vittoria,\textsuperscript{1} and V. G. Harris\textsuperscript{1}

\textsuperscript{1}Center for Microwave Magnetic Materials and Integrated Circuits and Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115 USA
\textsuperscript{2}Key Laboratory of Nano-Fabrication and Novel Devices Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029 People’s Republic of China

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The high-rate reactive ion etching of c-axis oriented quasi-single-crystal barium hexaferrite (BaM) films, deposited on 6-H silicon carbide (0001) substrates, has been demonstrated. Arrays of BaM columns, having diameters of 1–4 \(\mu\)m and sharp vertical walls, were etched from BaM films at rates as high as 75 nm/min using an optimized sulfur hexafluoride and methyl trifluoride (SF\textsubscript{6}:CHF\textsubscript{3}, 3:1) gas mixture. Lateral features as small as 43 nm were fabricated and imaged.

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It has been a long-standing goal of the microwave electronics community to integrate microwave passive devices (e.g., circulators, isolators, phase shifters, filters, etc.) with semiconductor device platforms. Such an achievement would meet the demands of increasing systems integration, while concomitantly reducing device profile, volume, and weight.\textsuperscript{1} Realizing practical integration relies upon two key technological advances: (i) the growth of oriented, high crystal quality magnetic oxide films on semiconductor substrates and (ii) the patterning of magnetic oxide films into device and integrated circuit structures. The processing of semiconductor film structures, including film deposition and patterning, has been well established, while similar processing of magnetic oxide film structures on semiconductor substrates remains a significant challenge. Previously, we have demonstrated the growth by pulsed laser deposition of c-axis oriented, quasi-single-crystal, barium hexaferrite (BaM) (i.e., BaFe\textsubscript{12}O\textsubscript{19}) films on wide-band-gap semiconductor substrates, SiC\textsuperscript{2–4} and GaN.\textsuperscript{5} Using such films as seed layers for growth by liquid phase epitaxy,\textsuperscript{6–9} films of more than 100 \(\mu\)m can be realized. This approach provides a reasonable pathway to integrating ferrite films, having the necessary thickness and crystal quality for microwave devices, with semiconductor platforms. Alternatively, the patterning of near- and submicron features in BaM and other ferrites has received considerably less attention and remains a significant challenge in realizing practical oxide-based microwave electronics. It is widely acknowledged that the depth control afforded by wet etching of ferrites is a key limitation.\textsuperscript{10} Attempts at dry etching ferrite materials, using Ar ions and laser thermal etching,\textsuperscript{10–13} resulted in severe lateral overetching and excessive film damage. In addition, no isotropic etching processes can reliably provide submicron lateral features.

The BaM films used in this study had thicknesses ranging from 0.5 to 2.0 \(\mu\)m and were grown by pulsed laser deposition (PLD) on single crystal 6-H SiC substrates. The details of the film growth are presented elsewhere.\textsuperscript{2–4} Due to the alignment of the crystallographic c-axis perpendicular to the film plane together with low microwave loss, such films are uniquely suited for many microwave device applications. However, the demagnetization energy inherent in thin films acts to align the spontaneous magnetization vector along the film plane, thus requiring large bias magnets to polarize and saturate the ferrite film for device operation. Bias magnets used in conventional passive devices are often heavy and voluminous constructs that limit attempts at planar integration. In realizing self-biased microwave passive devices, we propose the patterning of BaM films into arrays of cylindrical pillars. The demagnetizing field of the columns is expected to reduce the demagnetizing energy of the film and assists in the realignment of the spontaneous magnetization along the long axis of the columns. Additionally, a pillar array may also be used as a seed layer in the growth of thicker films by liquid phase epitaxy having unique and favorable microstructure. In this letter, the high-rate reactive ion etching of c-axis oriented quasi-single-crystal barium hexaferrite films, deposited on SiC substrates, is reported. BaM columns, having diameters of 1–4 \(\mu\)m and sharp vertical walls, were etched from BaM films at rates as high as 75 nm/min using SF\textsubscript{6} and CHF\textsubscript{3} gas mixtures. High resolution etching of lateral features as small as 43 nm were realized.

The etching experiments were performed using an ICP-98A system at the Institute of Microelectronics, Chinese Academy of Sciences. Before etching, optical lithography was performed to transfer the photomask test pattern to the photoresist (Shipley AZ5214-E). The depths of the pillars were measured after the dry etching process using a Veeco Dektak surface profilometer. The estimated error in the depth profile was \(\sim\)20 nm, which was considered in the estimated etch rate uncertainty.

In the reactive ion etch (RIE) process, the following three important parameters were optimized: (i) the process gas mixture, (ii) the chamber pressure, and the (iii) capacitive electrode rf power. During the film etching, the plasma chamber was evacuated to a dynamic vacuum of \(\sim\)10\textsuperscript{–6} Torr, maintained by a gas flow of 240 standard cubic centimeter per minute in concert with the conductance of the CHF\textsubscript{3}/SF\textsubscript{6} gas mixtures, 3:1. The etching experiments were performed using an ICP-98A system at the Institute of Microelectronics, Chinese Academy of Sciences. Before etching, optical lithography was performed to transfer the photomask test pattern to the photoresist (Shipley AZ5214-E). The depths of the pillars were measured after the dry etching process using a Veeco Dektak surface profilometer. The estimated error in the depth profile was \(\sim\)20 nm, which was considered in the estimated etch rate uncertainty.

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turbomolecular pump. The sample holder was water cooled to maintain a fixed sample temperature of $\sim 27^\circ$ C to minimize thermally induced damage to the film sample. An initial gas mixture of CHF$_3$/Ar (5:2), similar to that used in conventional SiO$_2$ etching, as well as CHF$_3$ alone, resulted in only slight etching of the sample and little removal of film mass. The BaM film was only effectively etched after the CHF$_3$ was mixed with SF$_6$. The optimal ratio of CHF$_3$ :SF$_6$, 1:3 was achieved through the systematic variation of gas mixtures and repeated evaluation of the etched patterns. The dependency of the etch rate to gas mixture is illustrated in Fig. 1. During measurements, the electrode rf power was maintained at 160 W. These results indicate that the presence of SF$_6$ was critical and acted as the primary reactive gas. We postulate that the SF$_6$ gas produced most of the ions and erosive neutrals, which were dissociated in the plasma environment to form atomic fluorine. Atomic fluorine in turn reacted with the BaM film to form volatile BaF$_x$ and FeF$_x$ gas complexes that were exhausted by the vacuum system. However, when only SF$_6$ gas was employed, the etch rate remained lower than that of the CHF$_3$ :SF$_6$ gas mixtures. This indicates that the CHF$_3$ was not only a buffer gas that maintained plasma stability but also provided additional energetic ions that enhanced the ionization of the SF$_6$ molecules.

In a second study, using an optimized 1:3 CHF$_3$/SF$_6$ mixture, the electrode rf power was varied to study its impact upon the etching profile. For each trial, etching was performed for a total of 5 min., as a function of electrode rf power. The etch rate was determined and plotted in Fig. 1(b). From these data, the etching threshold power was determined to be $\sim 60$ W, with a maximum etching rate of $\sim 87$ nm/min, corresponding to $\sim 240$ W of rf power. However, the application rf power greater than $\sim 200$ W resulted in the over etching of patterned sidewalls. The maximum rf power that resulted in high etch rates and high quality etched structures was $\sim 160$ W.

Figures 2(a)–2(c) are scanning electron microscopy (SEM) images of the top view (a), side view (b), and expanded view of one pillar consisting of a BaM cylinder with height to diameter aspect ratio of 0.2 having a photoresist cap on the surface (c). The “frost” on the element is a thin PtPd coating used to reduce fluorescence during SEM imaging. Top view SEM image of a test pattern designed to evaluate minimum lateral features (d). An expanded view of the minimal lateral feature of $\sim 43$ nm (at the necked region) (e).

FIG. 1. The etch rates of BaM films as a function of gas mixtures (a) and rf power (b). The data in panel (a) were collected using an rf power of 160 W.

FIG. 2. Top-view SEM image of the patterned BaM film array consisting of $\sim 3$ $\mu$m diameter pillars at a $\sim 4$ $\mu$m center-to-center spacing (a). Film was etched using an optimal gas mixture and rf power. Side-view SEM image of the same sample (b). An expanded view of one pillar consisting of a BaM cylinder with height to diameter aspect ratio of 0.2 having a photoresist cap on the surface (c). The “frost” on the element is a thin PtPd coating used to reduce fluorescence during SEM imaging. Top view SEM image of a test pattern designed to evaluate minimum lateral features (d). An expanded view of the minimal lateral feature of $\sim 43$ nm (at the necked region) (e).

FIG. 3. Hysteresis loops, as normalized magnetization vs applied magnetic field in Oe, for the as-deposited film sample (solid line) and etched film after annealing (dashed line). The lines correspond to the slope of the loops as they pass through remanence and qualitatively reflect the sample’s demagnetizing energies.
TABLE I. Demagnetizing fields ($H_d$), coercive fields ($H_c$), and demagnetizing factors ($N$) of as-deposited BaM film, after etching, and after etching followed by a heat treatment. Note: $\% \Delta$ represents percent change from as-deposited condition. $N_c$ was approximated using the oblate ellipsoid model, $N_c = m^2/(m^2-1)[1 - (1/|m^2-1|^{1/2})\arcsin(m^2-1)^{1/2}/m]$, where $m$ represents aspect ratio of pillar.

<table>
<thead>
<tr>
<th></th>
<th>$H_d(% \Delta)$ (Oe)</th>
<th>$H_c(% \Delta)$ (Oe)</th>
<th>$H_c(% \Delta)$ (Oe)</th>
<th>$N_c(% \Delta)$</th>
<th>$N_c(% \Delta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited film</td>
<td>3886</td>
<td>1600</td>
<td>189</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>Etched film</td>
<td>3137</td>
<td>2000</td>
<td>332</td>
<td>0.75</td>
<td>0.78</td>
</tr>
<tr>
<td>Etched film after anneal</td>
<td>3100</td>
<td>756</td>
<td>39</td>
<td>0.75</td>
<td>0.77</td>
</tr>
</tbody>
</table>

In summary, the mixture of SF$_6$ and CHF$_3$ was found effective in the reactive ion etching of $M$-type barium hexaferrite. The presence of CHF$_3$ was shown to be important to both the etching rate and the quality of vertical sidewall profiles. The optimum gas mixture was a ratio of one part CHF$_3$ to three parts SF$_6$, with an electrode rf power of 160 W. These conditions lead to the maximum effective etch rate of $\sim 75$ nm/min and the patterning of nanoscale features of less than 50 nm in films as thick as 2 $\mu$m. The magnetic properties, especially those reflecting magnetic loss, were shown to degrade with etching. However, postetching heat treatments showed that the magnetic properties were recovered and even improved relative to their virgin state. The high rate etching of magnetic oxides, and specifically microwave ferrites as demonstrated here, is an essential advancement that enables fabrication of planar microwave devices and their ultimate integration with semiconductor integrated circuit platforms.

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10U.S. Patent No. 4,875,970 (29 October 1989).